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# Experimental study of Cu isotope fractionation during the reaction of aqueous Cu(II) with Fe(II) sulfides at temperatures between 40 and 200 °C.

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## Abstract

We present results of an experimental study on Cu isotope fractionation during the reaction of aqueous Cu(II) with Fe(II) sulfides: pyrrhotite and pyrite. The reaction was investigated under a range of experimental conditions, including time, temperature, initial Cu concentration in the solution, presence of a complexing ligand (acetate), and mineral to solution ratio.

The reaction develops a series of mixed Cu-Fe and Cu sulfides. Cu isotope composition of reacted solutions and minerals determined by MC-ICP-MS attests to significant isotope fractionation that accompanies this reaction. The measured  $\Delta^{65}\text{Cu}_{\text{solution-minerals}}$  values range from 1.97 to 3.23 ‰  $\delta^{65}\text{Cu}$ , with an average of 2.64 ‰  $\delta^{65}\text{Cu}$ . Observed shifts in Cu isotopic composition with reaction progress are explained by preferential transfer of the lighter Cu isotope,  $^{63}\text{Cu}$ , from solution into the mineral. It is proposed that Cu(II) to Cu(I) reduction step is the key control of the magnitude of observed isotope fractionation, while other factors, such as presence of complexing ligands, play minor role. This kinetic fractionation process is, however, affected by some degree of isotopic exchange and equilibration between Cu in the neoformed minerals and in the solution, at least in samples

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representing higher reaction extent. The results from 150 and 200 °C runs suggest that significant isotope fractionation occurs even at these elevated temperatures ( $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  above 2 ‰  $\delta^{65}\text{Cu}$ ).

The results of this study suggest that the reaction of aqueous Cu(II) with Fe(II) sulfides may be an important process in generating depleted  $\delta^{65}\text{Cu}$  signatures found in Cu-rich sulfides formed at low temperatures, such as sea-floor hydrothermal vents or sediment-hosted stratified copper deposits.

*Keywords:* Cu, isotope fractionation, ferrous sulfides, alteration, low temperature

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## 1. Introduction

Stable Cu isotopes are known to undergo significant fractionation in nature spanning at least 10 ‰ as  $\delta^{65}\text{Cu}$  (Walker et al., 1958; Shields et al., 1965; Gale et al., 1999; Zhu et al., 2000). The advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) over the last decade has reduced analytical uncertainties on  $\delta^{65}\text{Cu}$  to below 0.1 ‰ ( $2\sigma$ ). As a consequence of this increased precision, Cu isotope systematics may provide new insights into the complex processes associated with metal cycling in the crust and the formation of metalliferous ore deposits. However, fractionation mechanisms responsible for the observed spread in natural Cu isotope compositions are still poorly understood, and need to be identified and quantified.

Primary Cu-rich sulfide minerals formed at high temperatures in igneous, skarn and high-temperature hydrothermal deposits, for example, are characterised by a relatively restricted range of Cu isotope compositions clustering about  $\delta^{65}\text{Cu} = 0$  ‰ ( $\pm 1$  ‰ – calculated with respect to the NIST SRM-976 standard), which is believed to represent the bulk Earth composition (Zhu et al., 2000; Larson et al., 2003; Mason et al., 2005; Markl et al., 2006; Mathur et al., 2009; Weiqiang et al., 2009). In contrast, lower temperature, secondary Cu-rich sulfides from hydrothermal vent deposits and stratified sediment-hosted deposits are typically depleted in  $^{63}\text{Cu}$  with  $\delta^{65}\text{Cu}$  values as low as  $-3.4$  ‰ (Rouxel et al., 2004; Markl et al., 2006; Asael et al., 2007).

A commonly observed mineralogical feature in low-temperature Cu-Fe and Cu sulfides is the progressive replacement by mineral phases increasingly rich in Cu. This type of mineral replacement is well documented in both hydrothermal (Duckworth et al., 1995; Knott et al., 1995; Butler et al., 1998)

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and stratified sediment-hosted (Huyck and Chorey, 1991; Sawlowicz, 1992; Bechtel et al., 2001; McGowan et al., 2006) Cu deposits. Because of their economic importance, the formation of Cu-rich sulfides at low temperatures has been a subject of experimental studies over the last century (Zies et al., 1916; Young and Moore, 1916; Schouten, 1934; Roberts, 1961, 1963; Rickard, 1970, 1972, 1973; Walsh and Rimstidt, 1986; Cowper and Rickard, 1989; Rickard and Cowper, 1994; Luther et al., 2002). The results of recent experiments (Cowper and Rickard, 1989; Rickard and Cowper, 1994) suggest that the reaction of Cu(II) solutions with Fe(II) sulfides (pyrrhotite, mackinawite and pyrite) at low and moderate temperatures is an important pathway for the formation of mixed Cu-Fe and Cu sulfides. By reacting aqueous Cu(II) (at pH between 2 and 4.5) with Fe(II) monosulfides (pyrrhotite and mackinawite) Cowper and Rickard (1989) produced a succession of mixed Fe-Cu and Cu mineral phases (cubanite, chalcopyrite, bornite, covellite and digenite) characterised by increasing Cu content. In fact, these workers failed to synthesise chalcopyrite by any other previously reported reaction, such as direct precipitation from solution (Roberts, 1963), solid-state diffusion (Roberts, 1961), or the reaction of solid CuS with iron solutions (Walsh and Rimstidt, 1986).

Because of the potential importance of the reaction of Cu(II) solutions with Fe(II) sulfides in the formation of Cu-Fe and Cu sulfides at low temperatures, and their occurrence in Cu rich deposits with depleted  $\delta^{65}\text{Cu}$  signatures, we investigated the Cu isotope fractionation associated with this reaction in laboratory under controlled experimental conditions.

## 2. Experimental methods

Natural crystals of pyrrhotite (from Brazil) and pyrite (from Spain) were used in the experiments. Crystals were crushed, ground, and sieved into two fractions: 1 mm–250  $\mu\text{m}$  and above 1 mm. The pyrite contained small inclusions of hornblende (considered unreactive) and carbonate, which was removed by washing in 10 % HCl. The pyrrhotite was separated from impurities magnetically.

All chemical reagents used were analytical reagent grade. The water used was deoxygenated Milli-Q<sup>TM</sup> ( $\sim 18 \text{ M}\Omega\cdot\text{cm}$ ). Deoxygenation of water was achieved by vigorously sparging it with oxygen-free grade  $\text{N}_2$  for at least 45 minutes in order to replace dissolved  $\text{O}_2$ . Cu(II) sulphate pentahydrate was used for the preparation of 3175 ppm (0.050 M) and 500 ppm (0.008 M) Cu

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solutions. The solutions were prepared in a N<sub>2</sub>-filled anoxic glove box with either water or 0.20 M Na-acetate buffer at pH = 4.00. Prior to the start of the experiment the material was immersed in a 1:1 acetone-petroleum ether mixture to remove grease from the mineral surfaces. This was followed by a brief wash with deoxygenated, concentrated HCl in order to dissolve iron oxides. The acid wash was conducted in the glove box so as to minimise the potential for re-oxidation of the mineral surfaces.

The experimental set-up differed between lower-temperature runs (40, 80 and 100 °C) and higher-temperature runs (150 and 200 °C). For the lower-temperature experiments, 250 or 500 mg of the mineral material was weighed into glass ampoules (see Rickard (1997) for original reference), and 10 or 20 ml of Cu solution was added with an automatic pipettor. The glass ampoules were closed using Swagelok<sup>®</sup> valves and attached to a gas-manipulation manifold (see Rickard (1997)). The ampoule atmosphere was further purged with oxygen-free grade N<sub>2</sub> and sealed using a blow-torch. Sealed ampoules were left in an oven for the duration of the experiment at a constant ( $\pm 2$  °C) temperature, their contents being occasionally (typically once a day) agitated. In case of the higher-temperature runs, the material was weighed into an O-ring-sealed teflon vessel. The vessel was placed inside a steel pressure-vessel and filled with appropriate amount of water so as to assure pressure equalization between the insides of the teflon vessel and the steel vessel. The temperature of the steel vessel was raised to target temperature within a period of up to two hours and controlled ( $\pm 1$  °C) throughout the experiment using an assembly of thermocouples, heating tape and a digital (PID) controller. Throughout the experiment the content of the vessel was allowed to mix on a shaking table. At the end of the run, the steel bomb was quenched to room temperature with cold water within 10–15 minutes. The reacted crystals were separated from the solution by vacuum filtration using 0.45  $\mu\text{m}$  cellulose nitrate Whatman<sup>®</sup> filters. The collected mineral material was washed with water, dried and collected for Cu isotope analysis. The filtrate was quantitatively transferred into a 100 ml volumetric flask, acidified to pH $\approx$ 2 with HNO<sub>3</sub>, and made up to volume. 10 ml of the solution was sub-sampled for the determination of Cu and Fe. Slight molar excess of sulfide (as Na<sub>2</sub>S solution) was added to the remainder to quantitatively precipitate the metals. The solution was filtered through the 0.45  $\mu\text{m}$  membrane. Full recovery of Cu and Fe was assured by the addition of a few extra drops of sulfide solution while the experimental solution remained colourless. The membrane with Cu-Fe sulfide was freeze-dried and the precipitate was collected for Cu

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isotope analysis. The collection of aqueous Cu as solid mackinawite was chosen for easier and safer transport between the UK and Israel, where the Cu isotope measurements were conducted.

Procedural blanks for the experimental procedure were conducted with 500 ppm and 3000 ppm Cu solutions giving complete recovery of Cu within instrumental errors (3 % relative error – see section 3).

In the experiments the type of reacted mineral (pyrrhotite and pyrite), mineral mass (250 and 500 mg), reaction temperature (40, 80 and 100 °C), Cu concentration in the initial solution (500 and 3175 ppm), volume of the initial Cu solution (10 and 20 ml), and the duration of the experiment (7, 10, 14, 21, and 42 days) were varied. In addition, selected solutions were buffered to pH = 4.50 with 0.20 M Na-acetate. All samples were run as duplicates under the same experimental conditions. Table 1 gives a summary of the experimental run conditions for all experiments.

### 3. Analytical techniques

Final Cu and Fe concentrations were measured in experimental solutions. Cu was determined spectrophotometrically using a modified procedure adopted from Zaki and Alqasbi (1981), by Atomic Absorption Spectrometry using a Varian Spectra AA-300, and by EDTA titration (0.01 M) at pH=5.5 (1 M Na-acetate buffer) using glycine cresol red as an indicator (magenta to green endpoint). Fe was measured by Atomic Absorption Spectrometry. The relative precision of Cu and Fe concentrations in the analysed solutions is  $\pm 3$  %.

The reacted mineral grains were mounted in an epoxy resin and polished to provide smooth cross-sectional surfaces. These were studied by reflected light optical microscopy to determine the produced mineral phases. Reaction zones on a  $\mu\text{m}$ -scale were investigated by scanning electron microscopy with a Philips XL30CP energy dispersion system.

Experimental Cu(II) solutions precipitated as covellite, and their corresponding minerals were dissolved in 10 ml of 0.1 M  $\text{HNO}_3$ . Prior to mass spectrometric measurement, samples were column purified using the procedure of Maréchal et al. (1999). The solutions were analysed for Cu and Fe contents by ICP-AES. Cu isotopic composition was determined using a Nu Plasma<sup>TM</sup> MC-ICP-MS at the Geological Survey of Israel in Jerusalem, Israel. Depending on the current sensitivity of the instrument, samples were introduced as 0.2–1 ppm Cu solutions in 0.1 M  $\text{HNO}_3$  using an Aridus sam-

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ple introduction system with aerosol desolvation. The instrumental drift and mass discrimination were monitored and corrected for relative to the external SRM NIST 976 Cu standard with standard-sample-standard bracketing technique, and by using Ni internal standard. Each measurement consisted of one block of 25 analyses, where precision was routinely tested by running the SRM NIST 976 Cu standard. Details of the mass spectrometric measurement and solution matrix corrections are given in Asael et al. (2007). It should be noted, that occasional isotopic shifts were encountered during the analytical work; these shifts are discussed in the Results section.

#### 4. Results

The experimental run conditions, measured Cu isotope fractionations, and Cu and Fe concentrations in solutions are presented in Table 1. Measured Cu concentrations in all experimental solutions are below their respective starting values. Considering that no Cu was lost from the system (see procedural blanks in section 2), this indicates that a mass transfer of Cu from the solution into the reacting mineral has occurred. The reacted Cu is expressed as a difference between the initial and final Cu concentrations in the solution, and presented as percent drop with respect to the initial concentration. The 1–100 % range of reacted Cu in analysed samples testifies to a varying degree of solution-to-mineral Cu transfer. This, in turn, is primarily a function of the duration and temperature of the run, as well as the ratio of the initial Cu content to the mineral mass used. It is observed that under the same experimental conditions, pyrrhotite reacts much more readily with aqueous Cu solutions than pyrite. For samples *M1a* to *M10b* Fe content was determined. As no Fe was initially present in the solution, it must derive entirely from the reacting Fe sulfide. Fe and Cu concentrations in solutions do not correlate in any obvious way.

Optical microscopy observations reveal mineral alteration of the original Fe sulfides (Figures 1 and 2).

The secondary Cu-Fe and Cu sulfides produced as a result of the reaction of aqueous Cu with solid Fe sulfides include chalcopyrite, bornite, covellite and digenite. The product mineral phases tend to either replace the original grains along the edges, cracks and cleavage surfaces as more or less continuous rims and layers (Figure 1(a), 1(b)), or form irregular “patches” of alteration (Figure 1(c), 1(d)). The greatest extent of alteration is seen in mineral parts of two samples for which we do not present isotopic data (because a

Table 1: Experimental run conditions, measured Cu isotope fractionations, and Cu and Fe concentrations in experimental solutions. All samples mass balance on  $\delta^{65}\text{Cu}$  of the initial Cu solution to within 0.20 ‰. Duplicate samples are denoted with a matching numeral, followed by the letter *a* or *b*.

Sample name	Mineral <sup>a</sup> reacted	Mineral mass [mg]	T [C]	Duration [days]	Initial Cu solution [ppm]	Cu solution volume [ml]	Final Cu <sup>b</sup> solution [ppm]	Reacted Cu [%]	Final Fe <sup>b</sup> solution [ppm]	$\delta^{65}\text{Cu}$ solution	$\delta^{65}\text{Cu}$ mineral	$\Delta^{65}\text{Cu}_{\text{solution}} - \text{mineral}$ <sup>c</sup>
M1a	Po	250	100	14	3175	10	1897	40	185	1.30	-0.67	1.97
M1b	Po	250	100	14	3175	10	1528	52	352	1.71	-0.55	2.26
M2a	Po	250	80	21	3175	10	2414	24	150	1.03	-1.35	2.38
M2b	Po	250	80	21	3175	10	2394	25	139	1.13	-1.29	2.42
M3a	Po	250	80	21	3175 <sup>d</sup>	10	1886	41	23	1.57	-0.89	2.46
M3b	Po	250	80	21	3175 <sup>d</sup>	10	2066	35	8	1.57	-0.95	2.52
M4a	Po	250	40	42	3175	10	2773	13	55	1.02	-1.73	2.73
M4b	Po	250	40	42	3175	10	2850	10	52	0.90	-1.80	2.70
M5a	Py	250	80	21	3175	10	2858	10	80	0.80	-1.76	2.56
M5b	Py	250	80	21	3175	10	2858	10	31	0.69	-1.82	2.51
M6a	Po	250	100	14	500	10	0	100	336	-	0.52	-
M6b	Po	250	100	14	500	10	0	100	312	-	0.59	-
M7a	Po	250	80	21	500 <sup>d</sup>	10	0	100	324	-	0.59	-
M8a	Po	250	80	21	500	10	24	95	203	3.07	0.42	2.65
M8b	Po	250	80	21	500	10	11	98	222	3.36	0.50	2.86
M9a	Po	250	40	42	500	10	346	31	41	1.23	-1.48	2.71
M9b	Po	250	40	42	500	10	336	33	44	1.41	-1.42	2.83
M10a	Po	250	100	7	3175	100	2394	25	95	1.12	-0.90	2.02
M10b	Po	250	80	10	3175	10	2537	20	74	1.26	-1.51	2.76
M11a	Py	250	200	1	3175	200	1580	50	82	2.01	-0.49	2.50
M11b	Py	250	200	1	3175	10	1626	49	109	1.93	-0.48	2.41
M12a	Po	250	150	1	3175	10	2489	22	17	1.22	-0.92	2.14
I1a	Py	250	100	14	3175	10	2858	6	-	0.73	-1.80	2.53
I1b	Py	250	100	14	3175	10	2858	8	-	0.85	-2.01	2.86
I2a	Po	500	100	14	3175	20	2540	14	-	1.02	-1.54	2.57
I2b	Po	500	100	14	3175	20	2540	18	-	1.08	-1.48	2.56
I3a	Po	500	100	14	3175	20	2540	11	-	0.91	-2.05	2.96
I3b	Po	500	100	14	3175	20	2540	11	-	0.89	-1.71	2.60
I4a	Py	250	40	42	3175	10	2858	1	-	0.54	-2.23	2.77
I4b	Py	250	40	42	3175	10	2858	1	-	0.70	-1.85	2.53
I5a	Po	500	40	42	3175	20	2540	6	-	0.50	-2.42	2.92
I5b	Po	500	40	42	3175	20	2540	5	-	0.77	-2.46	3.23
I6a	Po	500	40	42	3175	20	2540	4	-	0.61	-2.49	3.10
I6b	Po	500	40	42	3175	20	2540	4	-	0.58	-2.27	2.83

<sup>a</sup> Po - pyrrhotite, Py - pyrite

<sup>b</sup> relative error below 3 %

<sup>c</sup>  $\Delta^{65}\text{Cu} = \delta^{65}\text{Cu}_{\text{solution}} - \delta^{65}\text{Cu}_{\text{minerals}}$

<sup>d</sup> Runs buffered with 0.2 M Na-acetate to pH = 4.0



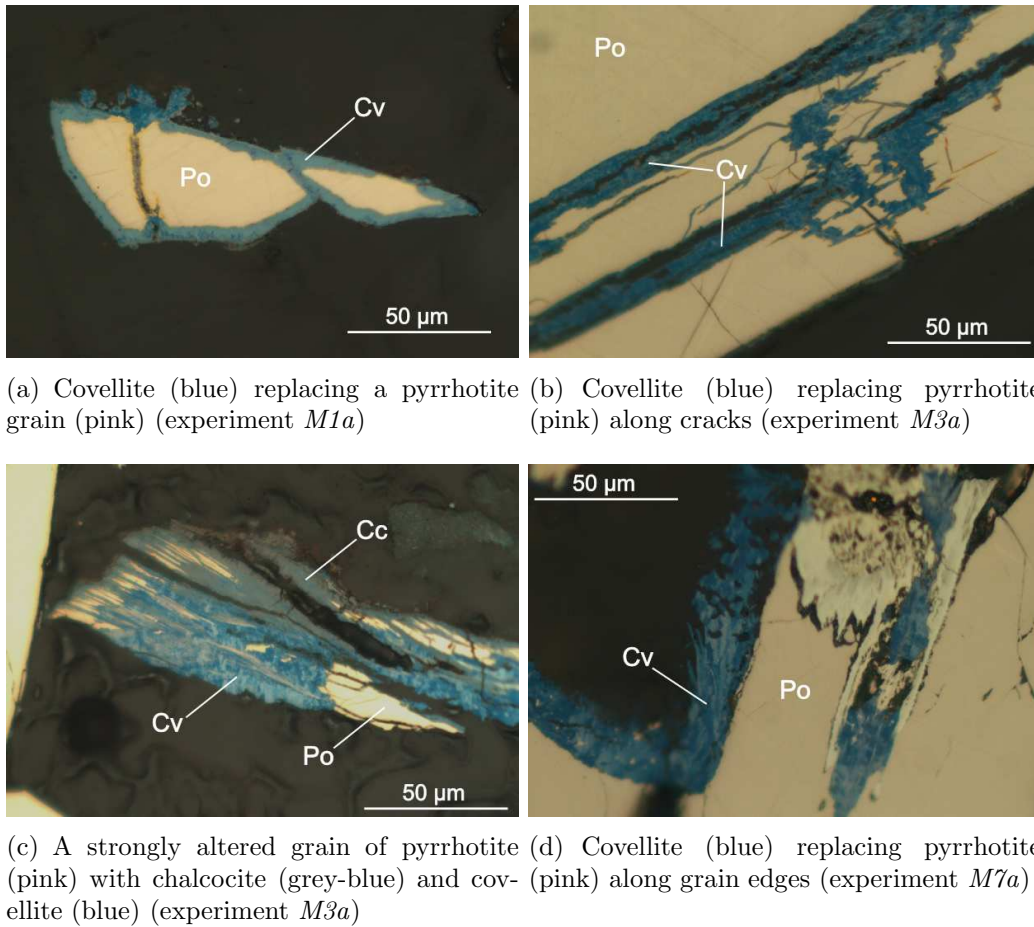
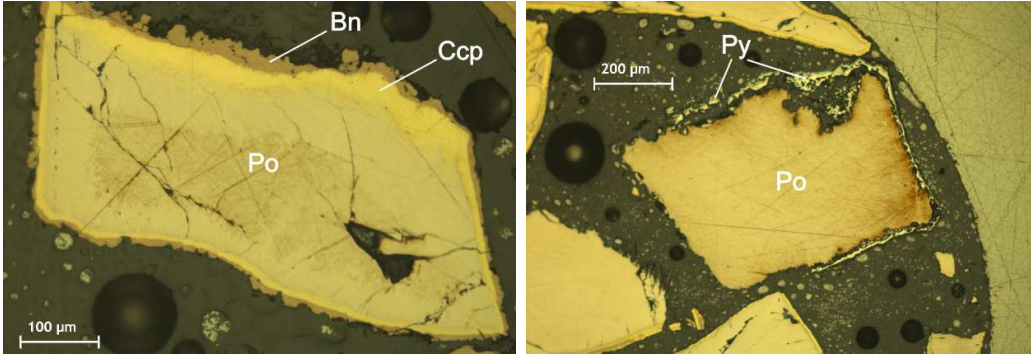


Figure 1: Optical images from reflected light microscopy of polished sections of experimental products showing pyrrhotite replacement by secondary Cu-Fe and Cu sulfides in the lower-temperature runs (40, 80 and 100 °C); pyrrhotite, *Po*, covellite, *Cv*, chalcocite, *Cc*.

satisfactory mass balance was not obtained). These samples were pyrrhotite grains run at 200 °C for 24 hours with initial Cu content of 3175 ppm, of which nearly all was reacted into the mineral. The mineral alteration found in these samples is strongest with bornite and chalcopyrite rims of up to 50  $\mu\text{m}$  thick (Figure 2(a)) and show signs of extensive pyrrhotite dissolution (Figure 2(b)). At their greatest extent, the alteration rims around pyrrhotite



(a) A partially altered grain of pyrrhotite (pink) with rims of chalcopyrite (gold-yellow) and bornite (brown) (b) A partially dissolved pyrrhotite grain (pink) with a secondary pyrite rim (light yellow)

Figure 2: Optical microscopy images of alterations in pyrrhotite reacted for 24 hours at 200 °C with initial 3175 ppm Cu solution and an almost complete reaction. Cu isotope data is not presented for this sample due to unsatisfactory mass balance obtained (pyrrhotite, *Po*, chalcopyrite, *Ccp*, bornite, *Bn*, pyrite, *Py*)

grains reacted at lower temperatures are much thinner at about 5  $\mu\text{m}$  (Figure 1(a)). The dominant portion of Cu appears to be incorporated into thin layers (typically 1–2  $\mu\text{m}$ ) of Cu-Fe and Cu sulfide minerals commonly found along cleavage and crack surfaces, which can readily be seen using electron scanning microscopy (Figure 3).

In agreement with the small extent of reacted Cu measured in runs with pyrite ( $\leq 10\%$ ), mineral alterations of this mineral are limited and restricted to dispersed small patches of covellite.

The analytical precision of Cu isotope measurement was 0.1 ‰  $\delta^{65}\text{Cu}$  (1 $\sigma$ ). A shift in the  $\delta^{65}\text{Cu}$  value of the initial Cu solution was occasionally observed over a period of two years (new aliquots prepared from the same batch of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). The shift covered a total range of -0.20–0.73 ‰ over that period, but was constant during any one analytical session, which

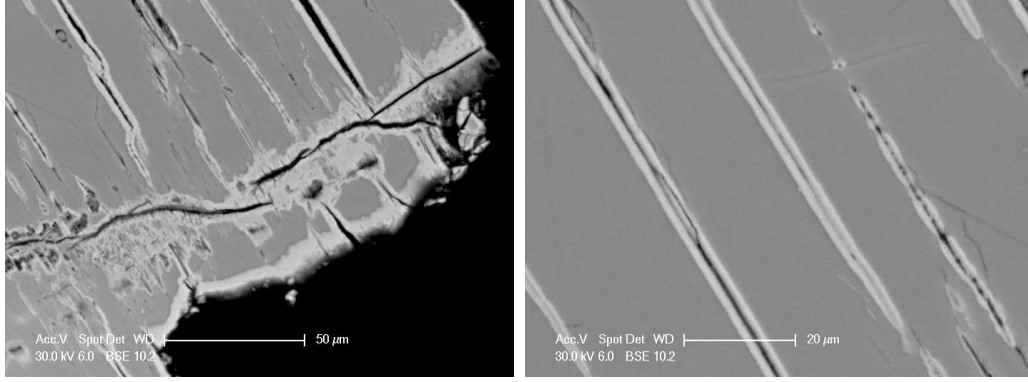


Figure 3: SEM images of pyrrhotite (grey) being replaced by covellite (white) in sample *M1b*

allowed for normalisation of the measured  $\delta^{65}\text{Cu}$  in samples against an arbitrary (operational) value of 0.56 ‰ for the initial Cu solution. As the shift only changed between sessions, we believe that it might have been affected by conditions in the source during sample extraction (e.g.: position of the torch and flow rate). Nevertheless, because of the constancy of the shift during an analytical session, it could not have affected the calculated  $\Delta^{65}\text{Cu}$  values. The normalisation was, however, needed for mass balance calculations, for which the isotope composition of the initial solution must be known. The solution-mineral pairs were mass-balanced for the initial  $\delta^{65}\text{Cu}$  according to:

$$\delta^{65}\text{Cu}_{sol,i} = \frac{(\delta^{65}\text{Cu}_{min,f} \cdot c_{min,f} + \delta^{65}\text{Cu}_{sol,f} \cdot c_{sol,f})}{c_{sol,i}} \quad (1)$$

where:  $c$  is concentration [ppm], and the subscripts  $sol$ ,  $min$ ,  $i$  and  $f$  stand for *solution*, *mineral*, *initial* and *final*, respectively. Note that:  $C_{min,f}$  is calculated as the difference between the starting and final concentrations in the solution:  $c_{sol,i} - c_{sol,f}$ . It assumes a closed system with no Cu loss, which is a reasonable assumption for a hermetically sealed glass ampoule. Cu content in the unreacted crystals of pyrite and pyrrhotite used in these experiments was determined by AAS to be 9 and 16 ppm, respectively. These low concentrations did not affect the mass balance and were ignored. All solution-mineral pairs mass-balanced according to Equation 1 to within  $\pm 0.2$  ‰  $\delta^{65}\text{Cu}$ . The deviation of the calculated mass balance from its theoretical value stems from experimental and analytical errors incurred during each experimental

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stage (such as sample handling, and elemental and isotopic measurements). As such, it represents the integrated experimental uncertainty, and can be used as a measure of the total (external) reproducibility of the experiments. Based on the  $\pm 0.2$  ‰  $\delta^{65}\text{Cu}$  deviation calculated for our samples, the propagated uncertainty on  $\Delta^{65}\text{Cu}$  is smaller than  $\pm 0.3$  ‰  $\delta^{65}\text{Cu}$ . Hence, we adopt the value of  $\pm 0.3$  ‰ as the best estimate of external reproducibility on the presented  $\Delta^{65}\text{Cu}$  values. A clear-cut check of system closure is provided by experiments which went to 100 % reaction (*M6a*, *M6b* and *M7a*). Since all the Cu from the solution must have been transferred into the corresponding minerals in these samples, the minerals should have acquired the Cu isotope composition of the initial solution. This is in fact true within the  $\pm 0.2$  ‰  $\delta^{65}\text{Cu}$  uncertainty (Table 1).

For all studied samples,  $\delta^{65}\text{Cu}$  values measured in the solutions are equal to or higher than the value of the initial solution (0.56 ‰  $\delta^{65}\text{Cu}$ ). Conversely, the  $\delta^{65}\text{Cu}$  values of the Cu and Cu-Fe sulfides are lower than or equal to that of the initial solution. With reaction progress, the solutions become increasingly isotopically heavy (increasing  $\delta^{65}\text{Cu}$ ), starting from the initial value of 0.56 ‰  $\delta^{65}\text{Cu}$ , and reaching the maximum of 3.36 ‰  $\delta^{65}\text{Cu}$  at 100 % reacted Cu. This trend is followed closely by the isotopic compositions in the corresponding mineral samples, where the lowest values (around -2.5 ‰  $\delta^{65}\text{Cu}$ ) are observed at the initial stages of the reaction, and, with the reaction progressing, they gradually climb up to reach the initial Cu isotope composition of the solution (0.56 ‰  $\delta^{65}\text{Cu}$ ) when reaction is complete. Both trends are linear and parallel (Figure 4). The separation between the *solution* and *mineral* lines is relatively constant and expresses the mean  $\Delta^{65}\text{Cu}_{\text{solution-minerals}}$  for all analysed samples (2.64 ‰  $\delta^{65}\text{Cu}$ ).

## 5. Discussion

Reactions between aqueous Cu(II) and pyrrhotite were previously studied experimentally by Cowper and Rickard (1989). The reaction with polished, oriented pyrrhotite surfaces produced a sequence of mineral phases progressively enriched in Cu at the pyrrhotite surface - similar to that observed in this study. It was found that the reaction was transport-controlled, with simultaneous inward-diffusion of Cu(II) from the solution into the mineral, and outward-diffusion of Fe(II). The reaction rate is essentially controlled by the rate at which Cu can be diffusively supplied to the reaction zone (Cowper and Rickard, 1989), where it must be reduced to Cu(I) prior to its incor-

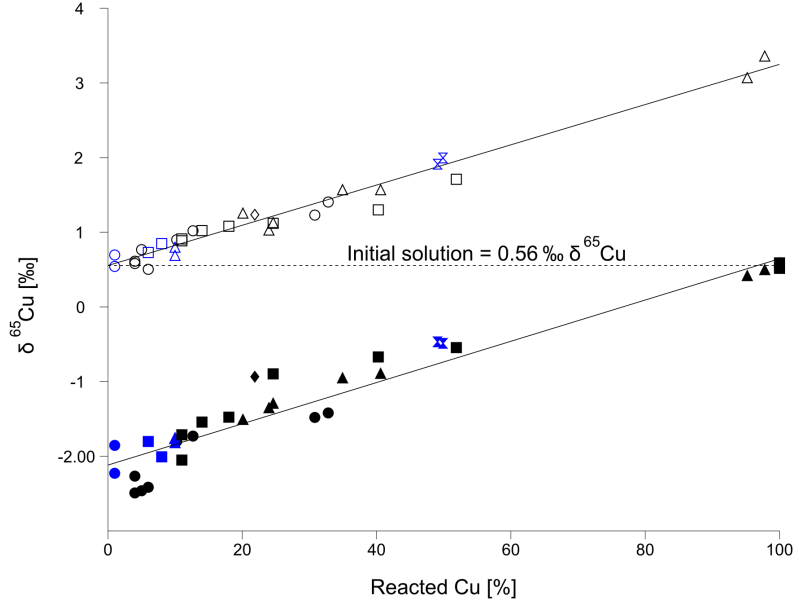


Figure 4: Measured  $\delta^{65}\text{Cu}$  in experimental solutions and the corresponding reacted minerals as a function of reacted Cu in the system [%]. Open and filled symbols represent the solutions and minerals, respectively. In black - pyrrhotite runs, in blue - pyrite runs. Circles, triangles, squares, diamonds and hour-glass symbols denote 40, 80, 100, 150 and 200 °C runs, respectively. The slanted lines are best fit to data and represent the mean trends of isotopic shift with reaction progress.

poration into the crystal structure (Vaughan and Craig, 1978; Luther et al., 2002; Patrick et al., 2004; Pearce et al., 2006). This mechanism is readily applicable to our pyrrhotite samples, and partly explains the observed mineral sequence. However, we propose an additional mechanism, whereby aqueous Cu(II) reacts with S(-II) and Fe(II) released into the solution by pyrrhotite dissolution. Evidence of extensive pyrrhotite dissolution can be seen in pyrrhotite reacted at 200 °C (Figure 2(b)) and, although not directly observed, limited dissolution must have occurred at lower temperatures, too. Covellite has a lower solubility product than pyrrhotite (Rickard and Luther, 2006) and equilibration of pyrrhotite with the solution leads to an increase in the dissolved S(-II) activity. This S(-II) activity results in an ion activity

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product for  $\{\text{Cu(II)}\}\{\text{S(-II)}\}$ , which is greater than the solubility product for covellite. The direct precipitation of covellite from solution is kinetically controlled by the rate of pyrrhotite dissolution, which is temperature dependent. We ascribe the localised, patch-like covellite mineralisation observed in the lower-temperature pyrrhotite runs to such direct precipitation from solution, where the reacting mineral additionally provides a convenient surface for crystal growth. We propose that the required Cu(II) reduction to Cu(I) takes place in the solution during condensation of polynuclear  $\text{Cu}_3\text{S}_3$  rings to  $\text{Cu}_4\text{S}_6$  and  $\text{Cu}_4\text{S}_5$  aqueous molecular clusters, which are isostructural with covellite and are building blocks for the formation of covellite (Luther et al., 2002). Attachment of these clusters at the mineral surface, rather than incorporation of aqueous Cu(II) species, may fractionate isotopically light Cu into the solid phase, and also account for the congruency between the fractionations measured in this study and those reported by Ehrlich and co-workers (Ehrlich et al., 2004) for the fractionation of Cu isotopes during the precipitation of CuS from aqueous solution. It is however acknowledged, that the specific step involving Cu(II) to Cu(I) reduction within the mechanisms is uncertain. Therefore, at present, Cu reduction at the mineral surface cannot be entirely ruled out. It is worth noting that, in this study, unlike in that of Cowper and Rickard (1989), no attempt was made to control the mineral surface orientation. Varying surface properties in grains showing multiple orientations may account for the proposed mixed mechanism of mineral formation, and may have contributed to observed spread in measured  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values from samples representing the same reaction temperature.

The observed relatively limited extent of aqueous Cu(II) reaction with pyrite is in agreement with slower reaction rate reported by Rickard and Cowper (1994). These authors found that, in contrast to pyrrhotite, the pyrite reaction with Cu(II) solution is surface-controlled and restricted mostly to high energy surface sites (edges, cracks, dislocations and crystal boundaries). The overall reaction rate is controlled by the Cu(II) to Cu(I) reduction step at the pyrite surface (Rickard and Cowper, 1994). The solubility of pyrite is far lower than that of covellite (Rickard and Luther, 1997) and direct precipitation of covellite from solutions is not expected to occur through pyrite dissolution alone.

Mechanistically, the isotope fractionation process between the Cu(II) solution and the formed Cu-Fe and Cu sulfides is explained by the transfer of the lighter Cu isotope,  $^{63}\text{Cu}$ , from the solution into the reacting mineral phase. As a result, the remaining solution becomes increasingly enriched

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in the heavier Cu isotope,  $^{65}\text{Cu}$ , as the reaction advances (Figure 4). Simultaneously, the corresponding reacting mineral, into which the lighter Cu isotope is incorporated, starts off with a depleted  $\delta^{65}\text{Cu}$  signature (the result of preferential enrichment in  $^{63}\text{Cu}$ ), which shifts towards heavier Cu isotope composition as the solution becomes isotopically heavier.

As can be seen from Table 1 the calculated  $\Delta^{65}\text{Cu}_{\text{solution-minerals}}$  values span the interval of 1.97 to 3.23 ‰  $\delta^{65}\text{Cu}$ , with a mean of 2.64 ‰  $\delta^{65}\text{Cu}$ . This is for all the studied samples, which represent a significant variety of experimental conditions. The total spread of about 1 ‰  $\delta^{65}\text{Cu}$  constitutes only half of the 2 ‰  $\delta^{65}\text{Cu}$  fractionation, which defines the lowest extent of observed isotope fractionation (sample *M1a*). It suggests that starting mineral type, initial solution Cu content, the ratio of mineral mass to the Cu solution volume, temperature and duration of the runs, as well as whether or not the initial Cu solutions were buffered with acetate have relatively limited impact on the measured  $\Delta^{65}\text{Cu}_{\text{solution-minerals}}$  values. This points to a common, underlying mechanism that accounts for the average fractionation of 2.64 ‰  $\delta^{65}\text{Cu}$ .

Cu isotope fractionation has been investigated experimentally in a number of studies. Equilibrium Cu isotope fractionation between different aqueous species is known to be of limited extent: Maréchal and Albarède (2002) studied equilibrium Cu isotope fractionation during aqueous Cu species partitioning between solution and an ion-exchange resin at 20 °C. The greatest measured fractionation found was  $0.67 \pm 0.04$  ‰  $\delta^{65}\text{Cu}$ . Similarly, Cu isotope fractionation during Cu mineral precipitation, which does not involve Cu oxidation state change is small: Maréchal and Sheppard (2002) reported that during slow precipitation of malachite ( $\text{Cu}(\text{II})_2(\text{OH})_2\text{CO}_3$ ) from Cu(II) aqueous solution the measured Cu isotope fractionation was  $0.20\text{--}0.38 \pm 0.04$  ‰  $\delta^{65}\text{Cu}$ . Likewise, Ehrlich et al. (2004) reported a fractionation factor of  $0.28 \pm 0.04$  ‰  $\delta^{65}\text{Cu}$  on precipitation of  $\text{Cu}(\text{OH})_2$  from  $\text{CuCl}_2$  solution.

In contrast to the above, the change in redox state of Cu has been demonstrated to be an important control of Cu isotope fractionation. For instance, the precipitation of aqueous Cu(II) from solution by KI was found to cause a  $\Delta^{65}\text{Cu}$  fractionation (between the solution and CuI precipitate) of about 4 ‰  $\delta^{65}\text{Cu}$  (Zhu et al., 2002). Also, precipitation of aqueous Cu(II) from solution by  $\text{Na}_2\text{S}$  to form covellite ( $\text{CuS}$ ) gave a comparable result of about 3 ‰  $\delta^{65}\text{Cu}$  mean fractionation (Ehrlich et al., 2004). This value compares well with the mean  $\Delta^{65}\text{Cu}_{\text{solution-minerals}}$  found in this study. Cu isotope compositions analysed from natural mineral samples representing different Cu

oxidation states also indicate that redox process are the key factor controlling the extent of the fractionation (Shields, 1965; Larson et al., 2003; Rouxel et al., 2004; Markl et al., 2006; Asael et al., 2007; Mathur et al., 2009; Kimball et al., 2009). Based on the above, we propose that the observed Cu isotope fractionation between aqueous Cu(II) and the reacting Fe sulfides is primarily generated during the Cu(II) to Cu(I) reduction step.

As seen in Figure 4, the change in  $\delta^{65}\text{Cu}$  composition of solutions and minerals follow a linear trend with reaction progress. Moreover, the separation between the *mineral* and *solution* trends, which represents the mean  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$ , is constant. Figure 5 presents the measured isotope composition of solutions and minerals plotted against fractionation trends calculated using the closed-system equilibrium and Rayleigh models (Criss, 1999). From the figure, it can be seen that although for samples representing

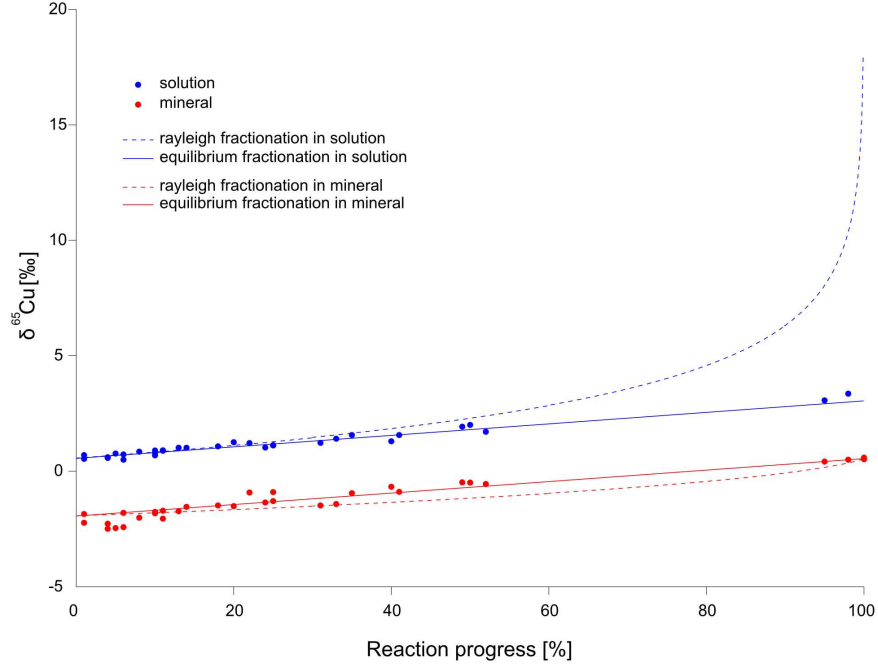


Figure 5:  $\delta^{65}\text{Cu}$  in experimental solutions and minerals as a function of reaction progress plotted against fractionation trends calculated using closed-system equilibrium and Rayleigh models. The dot sizes represent 0.2 ‰  $2\sigma$  precision.



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lower reaction extent it is not possible to discriminate between the two fractionation models, the solution samples at close to complete reaction clearly do not follow the trend defined by Rayleigh fractionation, and appear to agree with the equilibrium model. This is surprising considering that the fractionation process appears to be kinetic with unidirectional transfer of the lighter Cu isotope into the mineral phase, where it would be expected to be excluded from further reacting with the solution. True Rayleigh fractionation requires that the condensed phase is isolated, either chemically or physically from the reservoir from which it is created. We propose that this apparent inconsistency can be most easily explained by assuming that the Cu transferred into the mineral is not entirely prevented from later interactions with the solution. This is mainly due to the fact that as the Cu concentration in the solution drops, the kinetics of the reaction slows down, and a limited backwards transfer of Cu, due to solubility of Cu-Fe and Cu sulfides, may become significant. The isotopic shift is additionally amplified by the very small Cu content in the solution. It is also in accord with the higher temperatures and longer experiment run times required to achieve greater reaction extent. A consequence is that apparent equilibrium behaviour can be demonstrated by disequilibrium systems where exchange between isotopic reservoirs of differing sizes exists. Behaviour consistent with apparent isotopic equilibrium need not be an indication of true isotopic or chemical equilibrium.

Oxidative leaching of Cu from Cu and Cu-Fe sulfides has been shown experimentally to fractionate Cu isotopes. Aqueous Cu released from leached Cu(I) sulfides during abiotic oxidation has been demonstrated to be isotopically heavier than the starting composition of the mineral, while the leached mineral is lighter (Mathur et al., 2005; Fernandez and Borrok, 2009; Kimball et al., 2009). The  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  generated by this process can be as high as 2.74 ‰  $\delta^{65}\text{Cu}$  (Mathur et al., 2005). Oxidation of primary Cu-rich sulfides has been invoked as an explanation for Cu isotope fractionation observed in field studies at a variety of low temperature geological settings (Rouxel et al., 2004; Markl et al., 2006; Asael et al., 2007, 2009). This study suggests that the reaction of aqueous Cu(II) with Fe and Fe-Cu sulfides can provide an alternative explanation for the depleted Cu isotope signatures found in Cu-rich sulfides formed at low temperatures. We note that this process may be significant up to, and probably beyond, 200 °C, and so may be applicable to a variety of ore forming environments, and especially supergene environments.

As spread in the measured  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values is significant for

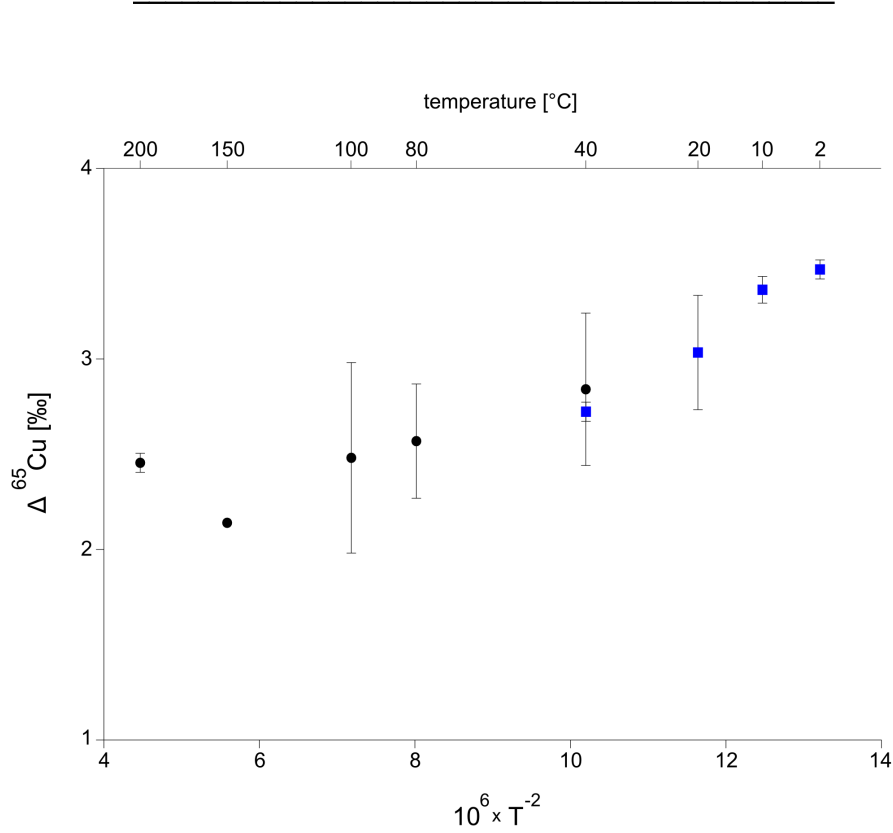


Figure 6: Temperature dependence of measured  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values and their relation to temperature dependence of  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  observed during direct copper sulfide precipitation from solution (Ehrlich et al., 2004). In black - this study, in blue - data from Ehrlich et al. (2004). Error bars represent maximum spread in measured  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values, while markers coincide with their arithmetic mean.

some samples, temperature dependence appears weak in Figure 6. Nevertheless, the inverse temperature relation of  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values reported from direct copper sulfide precipitation at temperatures between 2 and 40 °C (Ehrlich et al., 2004) is broadly confirmed by our data and extended up to 150 °C. This, again, suggests similar fractionation mechanisms despite overall differences in reaction style and kinetics. The two samples reacted at 200 °C, which lie outside of the trend, may reflect: (1) different fractionation processes at higher temperature, (2) different fractionation processes associated with the production of chalcopyrite and bornite as opposed to covellite, or (3) may reflect some contribution, which has occurred during quenching.

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Presently available data, however, do not permit us to discriminate among these possibilities, and further work is required on Cu isotope fractionation at temperatures  $>200$  °C.

## 6. Conclusions

The experiments conducted in this study demonstrate that the reaction of aqueous Cu(II) solutions with Fe sulfides produces a mineral alteration sequence whereby the original Fe sulfides are replaced by Cu-rich sulfide minerals of increasing Cu content. It is proposed that the Cu-rich minerals are formed by (i) Cu in-diffusion from solution into the mineral, and by (ii) direct precipitation of Cu sulfides from solution following partial dissolution of the original pyrrhotite and pyrite crystals.

The reaction generates significant Cu isotope fractionation, as evidenced by measured  $\Delta^{65}\text{Cu}_{\text{solution}-\text{minerals}}$  values between 1.97 and 3.23 ‰  $\delta^{65}\text{Cu}$ , and an average of 2.64 ‰  $\delta^{65}\text{Cu}$ . It is found that the measured Cu isotope fractionation is to a large extent independent of a variety of experimental conditions under which it was studied. This points to a common, shared fractionation mechanism for all investigated samples. It is proposed that Cu(II) to Cu(I) reduction is the main process responsible for the Cu isotope fractionation observed in this study. An important finding is that substantial fractionation (above 2 ‰  $\delta^{65}\text{Cu}$ ) can be generated by this reaction even at relatively high temperatures of 150 and 200 °C (2.14, and 2.41 and 2.50 ‰  $\delta^{65}\text{Cu}$ , respectively).

Mechanistically, the fractionation is explained by kinetic, unidirectional transfer of the lighter Cu isotope,  $^{63}\text{Cu}$ , from the solution into the mineral. Consequently, with reaction progress, increasingly depleted Cu signatures are developed in the mineral, and enriched signatures in the corresponding solution. However, the sequestration of  $^{63}\text{Cu}$  is not complete, allowing for a degree of back-exchange with the solution. This is evident for solutions of the most reacted samples (close to 100 % of reacted Cu), which follow a closed-system equilibrium fractionation line rather than the trend predicted by Rayleigh fractionation model. We explain this phenomenon by partial dissolution of the Cu-rich phases, which is stimulated by very low Cu concentrations in solutions, longer experiment run times and higher temperatures that characterise the most reacted samples. Although it cannot be stated unequivocally from available data, we presume that the same process may have affected the less advanced runs as well.

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The results of this work indicate that the reaction of aqueous Cu(II) solutions with Fe sulfides may be an important pathway for the formation of Cu-Fe and Cu sulfides at low temperatures in a variety of geological settings. The Cu isotope fractionations measured are in agreement with fractionations found in nature from sea-floor hydrothermal vents and stratified sediment-hosted Cu deposits. As such, it offers an alternative to oxidative leaching mechanism as an explanation for commonly found depleted Cu isotope signatures in secondary Cu-Fe sulfide minerals.

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